Catalyzed Reactions of Alkylaromatic Hydrocarbons
Dissolved in Supercritical Fluids

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INTRODUCTION

Partial oxidations of alkylaromatic compounds occur at below
600K through catalytic mechanisms that are partly free radical in
nature. These side chain oxidations and hydroxylations are usually
catalyzed homogeneously by transition metal complexes or mixtures of
metal salts with redox capabilities. Compounds of Co, Fe, and Mn are
examples; the catalytic mechanisms exhibit certain common features
(1-6). These are: (i) The ions have stable oxidation states
separated by +1, because chain initiation and other reaction steps
involve one-electron transfers; (ii) Once a reaction sequence (chain)
is initiated, thermal free-radical steps occur in parallel with
metal-catalyzed steps.

Alkylaromatics require less severe oxidizing conditions than
do alkanes because of their smaller (by ∼ 1 ev) ionization
potentials, and partially oxidized side chains deactivate the ring
for further reactions by this mechanism. Peroxides and
hydroperoxides are the primary products of these oxidations, but
these decompose to more stable products at temperatures above about
370K. As an example, consider the oxidation of toluene to
benzaldehyde/benzoic acid. Four proposed reaction networks are shown
in Figure 1. The initiation step involves electron transfer to Co^{3+},
suggesting that the trivalent ion is necessary for catalysis.
However, the divalent ion reacts in several benzoperoxy decomposition
steps, and in practice only small amounts of Co^{3+} are necessary.

An alternative to these liquid-phase processes is to use a
supercritical fluid (SCF) phase to contact solid analogs of the
homogeneous catalysts. Considering the above example of toluene
oxidation, the use of an SCF phase would result in a homogeneous
mixture and the removal of solubility limitations on O_2. SCF
mixtures have better mass transfer characteristics than typical
liquids, and rapid reaction quenching of highly exothermic oxidations
is possible by a pressure letdown from the SC region. A staged
pressure letdown engenders another benefit, that of fractionation of
reactants and products, eliminating the need for more complex
downstream separations. Therefore it appears possible to exploit the
capabilities of a SC mixture to provide a reaction medium for an
entire class of what would normally be liquid phase oxidations. We
are currently examining such catalytic oxidations in $SCF-CO_2$ for
upgrading model coal liquid compounds that result from SCF extraction
or flash hydropyrolysis processes. There are indications that
alkylaromatic side-chain partial oxidation, which we have already
demonstrated at SC conditions (7), will enhance the desired cracking
reactions. For example, hydroxy groups ortho or para to methylene
bridges facilitate bridge-bond rupture by allowing formation of a
lower energy keto-enol tautomer intermediate; the half-life of the
cleavage is reduced by over an order of magnitude (8). The presence
of water causes cleavage of ether linkages to alcohols, which has

been observed for guaiacol pyrolysis at SC conditions (9). An example of these and similar reactions as applied to actual coal liquids is the autoxidation followed by anaerobic thermolysis of SRC in quinoline (10). The yield to combustion products at 388-453K was less than 10%.

RESULTS AND DISCUSSION

Preparing SCF-Aromatic Hydrocarbon Mixtures
Figure 2 gives the P-T diagram for a mixture of toluene and carbon dioxide as constructed from experimental data (11) and the Peng-Robinson equation of state (12), with the critical locus for a binary mixture computed by the algorithm of Heideman and Khalil (13). The TP-CP curves (1 = carbon dioxide and 2 = toluene) represent the vapor P curves for the pure liquids, from their triple points to their critical points. At point O the three-phase line ends (the liquid phases become identical) and the critical locus extends to CP_2 of pure toluene. Point a is in the SCF (F) region, point b is on the critical locus, and point c represents typical operating conditions (473K, 100 atm) for the initial reaction studies. The P-X diagram at 473K is given in Figure 3. The SCF phase on the left of the diagram contains at least 20 mol% toluene. The feed to the reactor contained only 0.7% toluene and 2.0% O_2 and therefore constituted a single phase SCF mixture.

The phase diagrams for heavier molecules dissolved in SC-CO_2 indicate that their solubilities in the SCF phase will be much lower than that of toluene. For example the equilibrium mole fraction for phenanthrene in SC-CO_2 or CO_2-air mixtures at 473K and 100 atm was found to be less than 1%. However, the solubilities of either component of a binary solid mixture of aromatic hydrocarbons can be enhanced by up to 300% over its single component solubility (14). In addition, we have shown that by mixing a small amount (less than 10%) of a volatile hydrocarbon such as methanol or toluene with the SC-CO_2 it is also possible to greatly increase the solubilities of heavy aromatic hydrocarbons considered "nonvolatile". For example the solubility of DDT in CO_2 at 100 atm and 313K was shown to increase by more than an order of magnitude in CO_2 containing 6.7% methanol (15). These solubility enhancements due to solute-solute interactions should be sufficient to bring the SC-phase concentration of any aromatic single component or mixture into the typical range for vapor-phase oxidation catalysis, about 1-5 mol%.

Partial Oxidation Catalysis
The results of toluene oxidation experiments in a tubular fixed-bed reactor using an SC feed of CO_2, toluene, and air indicate that strongly acidic catalysts such as H-Y zeolite are inactive, and that, of the many supported metal oxides tested (Co, Mo, Co-Mo, and Ni-W oxides, supported on γ-Al_2O_3), the one whose active component was mostly CoO is the most active and also the most selective for partial oxidation to benzaldehyde and benzoic acid (7). Some results comparing this catalyst to a similar one containing mostly Co_3O_4 are given in Figure 4. The turnover numbers for partial oxidation are in the 10^{-7}-10^{-4}/s range, with the reactor operated differentially at conversions less than 2%; these rates are based on moles of total active metal.

The efficacy of the CoO compared to Co_3O_4 was also observed in a recent study of p-xylene oxidation in slurry reactors (16), and is probably a manifestation of the importance of the proper Co^{2+}/Co^{3+}

ratio in the catalysis (see Figure 1). The observed turnover numbers actually exceed those of previous studies where Co(II) homogeneous catalysts were used in the absence of initiators and electron transfer promoters (as in this work). For example, at 343K the observed turnover number for Co(II) acetate-catalyzed toluene partial oxidation is only 8.3 x 10^{-8}/s in pure acetic acid (17). Although rates as high as 0.01/s have been found at higher temperatures (1,18,19), these were measured in the presence of initiators and electron-transfer promoters such as soluble halides. We can adapt these technological developments to the high pressure process by incorporating such additives in the feed or the catalyst.

Effect of Total Pressure

The relatively high catalyst activities in the SCF oxidation process appear to be the result of a pressure effect. Holding the feed composition constant, we varied the total pressure in the reactor from about 80-140 atm, and observed the changes in the partial oxidation rate given in Figure 5. The more than twofold increase in rate might be explained by the effect of pressure on the concentration-based rate constant, as given by transition-state theory:

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T,x} = -\frac{\Delta V^{\ddagger}}{RT} + \left(\frac{1-n}{P}\right)\left[1 - \left(\frac{\partial \ln Z}{\partial \ln P}\right)_{T,x}\right] \qquad 1)$$

In the equation, $\Delta V^{\ddagger}$ is the difference in partial molar volumes of the activated complex and reactants, n is the molecularity of the reaction, and Z is the compressibility. Although this relation holds only for a single-step reaction, it can be used to roughly estimate the pressure effect here. Detailed calculations (20) using the Peng-Robinson equation of state and assuming a transition state thermodynamically similar to the product benzaldehyde [this assumption was tested for several bimolecular reactions of the type A + B → R for which the pressure variation was known, and was found to be adequate (21)] predicted an increase in a second-order rate constant of only about 30% for the pressure range of the data in Figure 5. It appears as if rate constant enhancement is not the most important consideration here.

Another possible explanation for the pressure effect is a pressure-dependent variation of O_2 concentration in the condensed "pore" phase of the catalyst. Work with microporous chars and zeolites has indicated that molecules can adsorb in multiple layers in porous media at pressures above the nominal mixture critical pressure, and that the adsorbed phase behaves almost liquid-like in terms of density and heat of adsorption (22,23). Referring to Figure 3, one would expect the capillary pores to be rich in toluene at low pressures but to become enriched in both air and CO_2 at increasing pressures. Because alkylaromatic oxidation reactions are typically of order zero to one in O_2, pore condensation phenomena could explain the rate increase; this idea is supported by the fact that the rate seemingly levels off near 140 atm, possibly indicating surface saturation.

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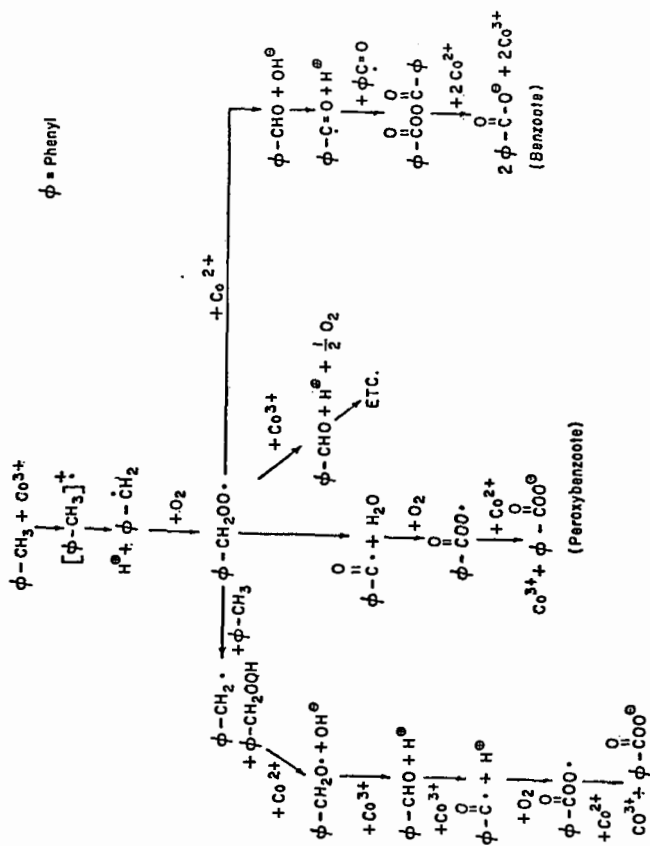   1959, 1953.

φ = Phenyl

$\phi-CH_3 + Co^{3+}$

$[\phi-CH_3]^+\cdot$

$H^\oplus + \phi-\dot{C}H_2$

$+O_2$

$\phi-CH_2OO\cdot$

$\phi-CH_2\cdot$
$+ \phi-CH_2OOH$
$+ \phi-CH_3$

$+ Co^{2+}$
$\phi-CH_2O\cdot + OH^\ominus$

$+ Co^{3+}$
$\phi-CHO + H^\oplus$

$+ Co^{3+}$
$\phi-\dot{C}=O + H^\oplus$

$+O_2$
$\phi-\overset{O}{\underset{\parallel}{C}}OO\cdot$

$+ Co^{2+}$
$Co^{3+} + \phi-\overset{O}{\underset{\parallel}{C}}OO^\ominus$

$+ Co^{2+}$

$\phi-\overset{O}{\underset{\parallel}{C}}\cdot + H_2O$

$+O_2$
$\phi-\overset{O}{\underset{\parallel}{C}}OO\cdot$

$+ Co^{2+}$
$Co^{3+} + \phi-\overset{O}{\underset{\parallel}{C}}OO^\ominus$ (Peroxybenzoote)

$+ Co^{3+}$
$\phi-CHO + H^\oplus + \frac{1}{2}O_2$
ETC.

$+ Co^{2+}$

$\phi-CHO + OH^\ominus$

$\phi-\dot{C}=O + H^\oplus$

$+ \phi C=O$
$\overset{O}{\underset{\parallel}{C}}=O$
$\phi-\overset{O}{\underset{\parallel}{C}}OO\overset{O}{\underset{\parallel}{C}}-\phi$

$+ 2 Co^{2+}$
$2\phi-\overset{O}{\underset{\parallel}{C}}-O^\ominus + 2Co^{3+}$ (Benzoote)

Figure 1. Reaction networks for toluene oxidation to benzaldehyde/benzoic acid, catalyzed by Co^{2+}/Co^{3+} in solution.
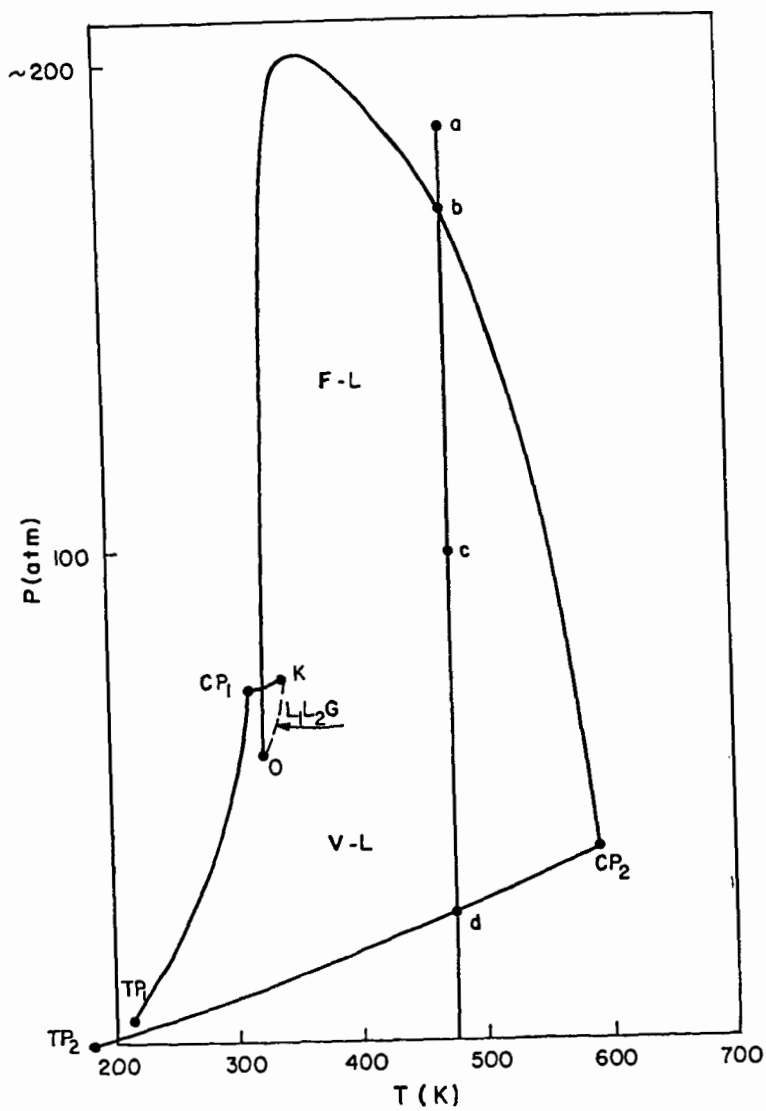
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Figure 2. P-T diagram for toluene and CO_2.

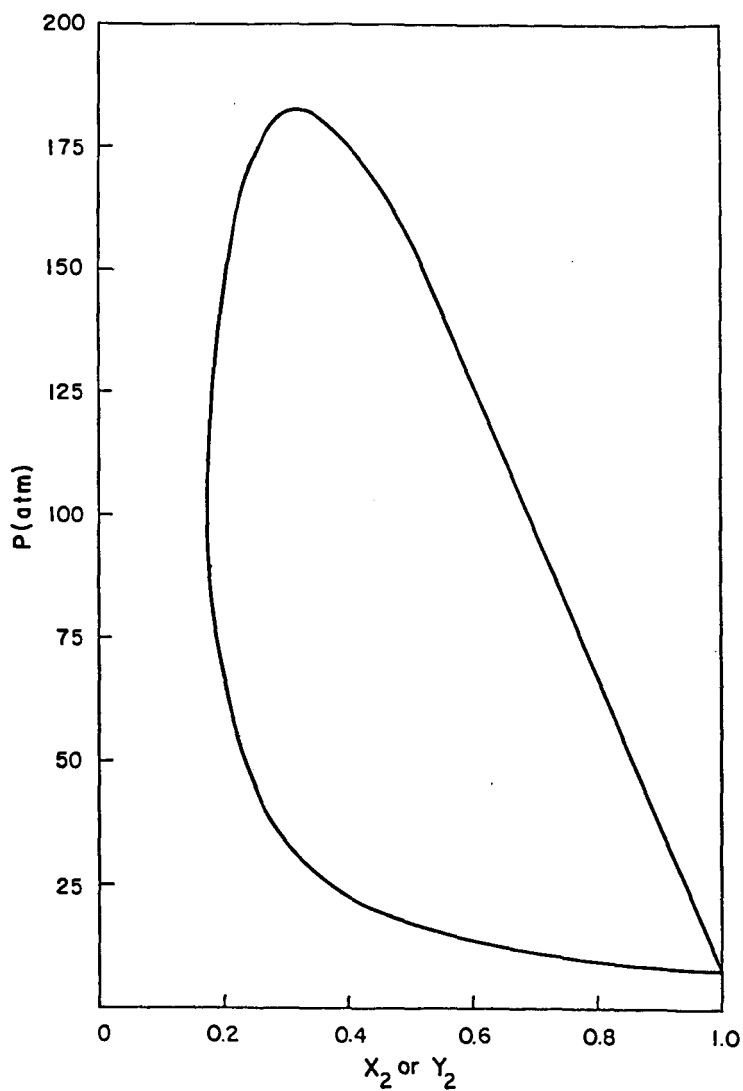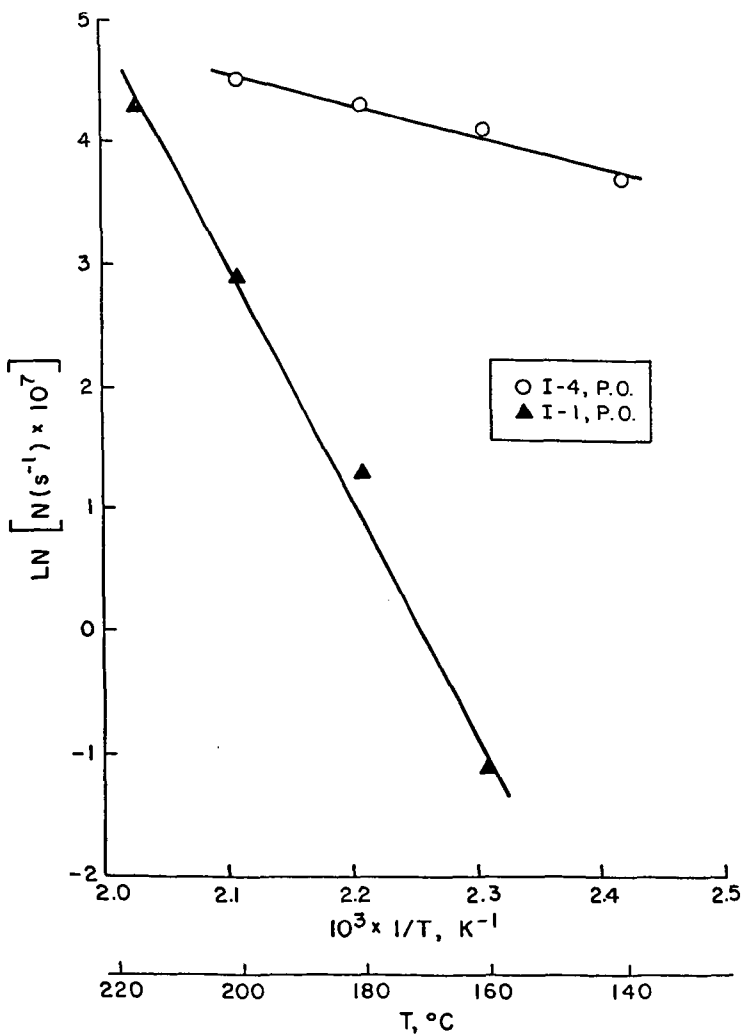Figure 3. P-X diagram for toluene and CO_2 at 200°C.

Figure 4. Turnover number for partial oxidation, for two supported Co oxide catalysts calcined at 400°C (I-1) and 200°C (I-4).
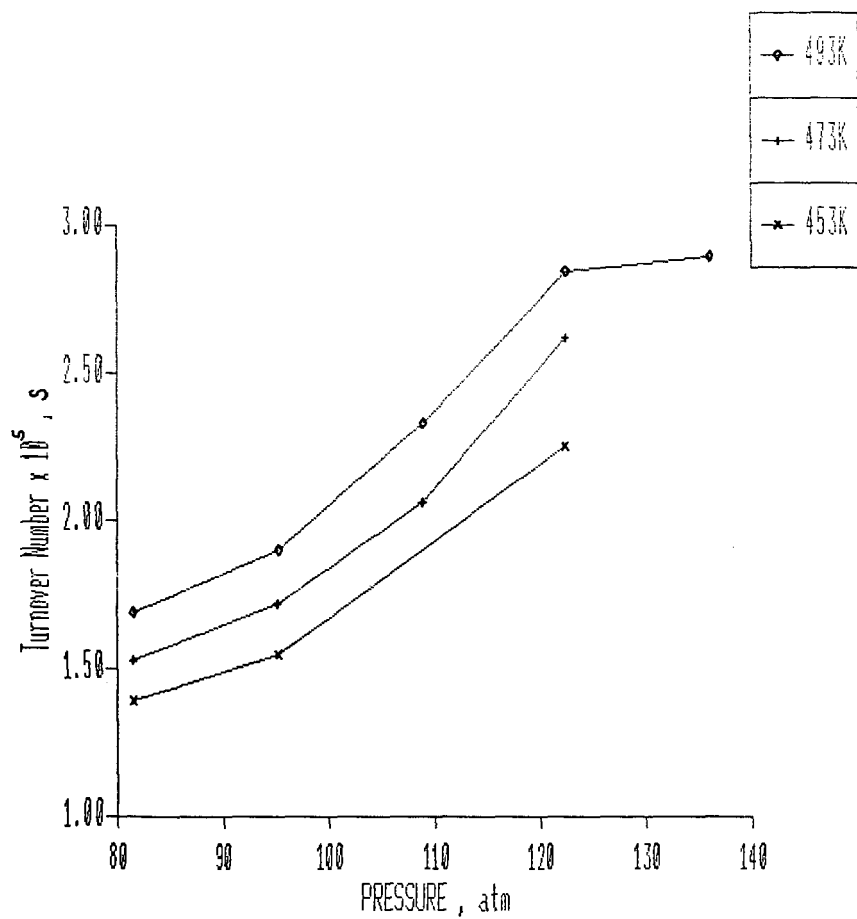
Figure 5. Turnover number per partial oxidation, for a supported Co oxide catalyst calcined at 200°C (catalyst I-4, 5% CoO).